

# Order parameters in the Verwey phase transition

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The Verwey phase transition in magnetite is analyzed on the basis of the Landau theory. The free energy functional is expanded in a series of components belonging to the primary and secondary order parameters. A low-temperature phase with the monoclinic P2/c symmetry is a result of condensation of two order parameters  $X_3$  and  $\Delta_5$ . The temperature dependence of the shear elastic constant  $C_{44}$  is derived and the mechanism of its softening is discussed.

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## I. INTRODUCTION

The mechanism of the phase transition in magnetite ( $\text{Fe}_3\text{O}_4$ ) at  $T_V = 122$  K, discovered by Verwey [1], has remained a big puzzle in the condensed matter physics for almost 70 years. Developments in experimental and theoretical methods during last years enabled to reveal subtle changes in the crystal and electronic structure below  $T_V$  [2, 3]. A simple charge ordering picture in which metal-insulator transition is induced by electrostatic interactions was replaced by a highly complex scenario in which lattice, charge, spin and orbital degrees of freedom are involved. Recent theoretical studies revealed the important role of the local electron interactions and orbital correlations in the  $t_{2g}$  states on iron ions [3].

The electronic interactions are complemented by the lattice deformation, which breaks the cubic symmetry and induces a low-temperature (LT) monoclinic phase driven by the electron-phonon interactions [4]. In the previous work [5, 6], we have obtained the phonon spectrum of magnetite (Fig. 1) using the *ab initio* computational technique [7]. We have identified two primary order parameters (OPs) at  $\mathbf{k}_X = \frac{2\pi}{a}(0, 0, 1)$  and  $\mathbf{k}_\Delta = \frac{2\pi}{a}(0, 0, \frac{1}{2})$  with the  $X_3$  and  $\Delta_5$  symmetry, respectively, which both play important role in the VT: (i) the  $\Delta_5$  mode is responsible for the doubling of the unit cell along the  $c$  direction in the monoclinic phase, while (ii) the  $X_3$  phonon induces the metal-insulator transition by its coupling to the electronic states near the Fermi energy [5]. Due to the electron-phonon interaction the above OPs are combinations of the electron (charge-orbital) and lattice components. This explains why the phonon soft mode has not been observed. Instead, low-energy critical fluctuations of OPs were found by the diffuse neutron scattering [9]. The condensation of the OPs below  $T_V$  explains the crystal symmetry change as well as the charge-orbital ordering.

The group theory predicts also secondary OPs, which do not effect the symmetry below  $T_V$  but modify the properties of magnetite close to a transition point. At the  $\Gamma$  point, the  $T_{2g}$  mode can be classified as the secondary OP, and its coupling to the shear strain explains the softening of the  $C_{44}$  elastic constant [10, 11]. The lowest  $T_{2g}$  optic mode, marked in Fig. 1, could contribute quantitatively to the free energy, but it does not play any significant role for the VT.

In this work, we introduce and analyze the Landau free energy for the VT, and discuss a solution corresponding to

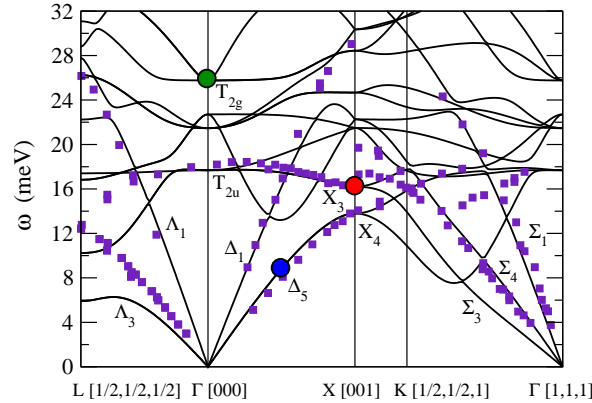


FIG. 1: The phonon dispersion curves of  $\text{Fe}_3\text{O}_4$  (solid lines) compared with the experimental points taken from Ref. [8]. The order parameters  $X_3$ ,  $\Delta_5$ , and  $T_{2g}$  are marked by circles.

the LT monoclinic phase. We derive also the temperature dependence of  $C_{44}$ .

## II. FREE ENERGY

The Landau free energy can be expanded into a series of the components of the OPs. The invariant terms describing couplings between the OPs were derived using the group theory methods [12]. The only nonzero components of the primary OPs  $X_3$  and  $\Delta_5$  are denoted by  $g$  and  $q$ , respectively. We include also the secondary OP with the  $T_{2g}$  symmetry ( $\eta$ ) and shear-strain ( $\epsilon$ ). The free energy can be written in the form [6]

$$\mathcal{F} = \mathcal{F}_0 + \frac{\alpha_1}{2}g^2 + \frac{\beta_1}{4}g^4 + \frac{\gamma_1}{6}g^6 + \frac{\alpha_2}{2}q^2 + \frac{\beta_2}{4}q^4 + \frac{\delta_1}{2}g^2q^2 + \frac{\alpha_3}{2}\eta^2 + \frac{\alpha_4}{2}\epsilon^2 + \frac{\delta_2}{2}\eta g^2 + \frac{\delta_3}{2}\epsilon g^2 + \delta_4\eta\epsilon, \quad (1)$$

where  $\mathcal{F}_0$  is the part of the potential, which does not change through the transition. We assume that  $\beta_1 > 0$ ,  $\beta_2 > 0$  and  $\gamma_1 > 0$  to ensure the stability of the potential at high temperatures. For the second-order terms we assume standard temperature behavior  $\alpha_i = a_i(T - T_{ci})$  near the critical temperature  $T_{ci}$  for  $i = 1, 2, 3$ , which would correspond to a continuous phase transition. The coefficient  $\alpha_4$  is the shear elastic constant at high temperatures ( $C_{44}^0$ ). The coupling between the primary OPs is biquadratic, between the secondary and primary OPs has the linear-quadratic form, and the coupling between the components of the secondary OP is of the bilinear type. Taking first derivatives of  $\mathcal{F}$  over all OPs we get

$$\frac{\partial \mathcal{F}}{\partial g} = g(\alpha_1 + \beta_1 g^2 + \gamma_1 g^4 + \delta_1 q^2 + \delta_2 \eta + \delta_3 \epsilon) = 0, \quad (2)$$

$$\frac{\partial \mathcal{F}}{\partial q} = q(\alpha_2 + \beta_2 q^2 + \delta_1 g^2) = 0, \quad (3)$$

$$\frac{\partial \mathcal{F}}{\partial \eta} = \alpha_3 \eta + \delta_4 \epsilon + \frac{\delta_2}{2}g^2 = 0, \quad (4)$$

$$\frac{\partial \mathcal{F}}{\partial \epsilon} = \alpha_4 \epsilon + \delta_4 \eta + \frac{\delta_3}{2}g^2 = 0. \quad (5)$$

The solution  $g = q = \eta = \epsilon = 0$  corresponds to the high-temperature cubic symmetry ( $Fd\bar{3}m$ ). From Eq. (3) we obtain the dependence between  $g$  and  $q$

$$q^2 = -\frac{\delta_1 g^2 + \alpha_2}{\beta_2}, \quad (6)$$

which has three possible solutions: (i)  $g = 0$  and  $q^2 = -\frac{\alpha_2}{\beta_2}$  if  $\alpha_2 < 0$  ( $Pbcm$ ), (ii)  $q = 0$  and  $g^2 = -\frac{\alpha_2}{\delta_1}$  if  $\alpha_2 > 0$  and  $\delta_1 > 0$  or  $\alpha_2 < 0$  and  $\delta_1 > 0$  ( $Pmna$ ), (iii)  $g \neq 0$  and  $q \neq 0$  ( $P2/c$ ). In the brackets we put the space group symbols, which characterize the low-symmetry phases. The solution (iii) which corresponds to the experimentally observed LT monoclinic phase requires simultaneous condensation of both primary OPs. The necessary condition for this is a negative value of  $\delta_1$ . Indeed, it has been established by the *ab initio* studies that the total energy is lowered when the crystal is distorted by both  $X_3$  and  $\Delta_5$  modes [6]. For  $\delta_1 < 0$ , Eq. (6) has a non-zero solution provided that  $|\delta_1|g^2 > \alpha_2$ . It implies that for  $\alpha_2 > 0$  ( $T > T_{c2}$ ), the phase transition occurs when the OP  $g$  exceeds a critical value  $\frac{\alpha_2}{|\delta_1|}$ , so it has a discontinuous (first-order) character.

From Eqs. (4) and (5) we get

$$\eta = \frac{\delta_3 \delta_4 - \delta_2 \alpha_4}{2\alpha_3 \alpha_4 - 2\delta_4^2} g^2 \equiv \lambda_1 g^2, \quad \epsilon = \frac{\delta_2 \delta_4 - \delta_3 \alpha_3}{2\alpha_3 \alpha_4 - 2\delta_4^2} g^2 \equiv \lambda_2 g^2, \quad (7)$$

which shows that  $\eta \neq 0$  and  $\epsilon \neq 0$  only if  $g \neq 0$ . Eliminating  $q$ ,  $\eta$  and  $\epsilon$  using Eqs. (6) and (7), the potential  $\mathcal{F}$  can be written as a function of  $g$

$$\mathcal{F} = \mathcal{F}'_0 + \frac{\alpha}{2}g^2 + \frac{\beta}{4}g^4 + \frac{\gamma_1}{6}g^6, \quad (8)$$

where the renormalized coefficients are

$$\mathcal{F}'_0 = \mathcal{F}_0 - \frac{\alpha_2^2}{4\beta_2}, \quad (9)$$

$$\alpha = \alpha_1 - \frac{\alpha_2 \delta_1}{\beta_2}, \quad (10)$$

$$\beta = \beta_1 - \frac{\delta_1^2}{\beta_2} + 2\alpha_3 \lambda_1^2 + 2\alpha_4 \lambda_2^2 + 2\delta_2 \lambda_1 + 2\delta_3 \lambda_2 + 4\delta_4 \lambda_1 \lambda_2. \quad (11)$$

The zero-order and second-order terms depend on the parameters belonging to the primary OPs. The secondary OPs modify only the forth-order term. In this notation, the solution of Eqs. (2)-(5), which minimizes the potential  $\mathcal{F}$  reads

$$g_o^2 = \frac{-\beta + \sqrt{\beta^2 - 4\gamma\alpha}}{2\gamma}, \quad q_o^2 = -\frac{\delta_1 g_o^2 + \alpha_2}{\beta_2}, \quad \eta_o = \lambda_1 g_o^2, \quad \epsilon_o = \lambda_2 g_o^2. \quad (12)$$

To study the softening of  $C_{44}$ , we have eliminated  $g$ ,  $q$ , and  $\eta$  using Eqs. (2), (3), and (4), and expressed the free energy as a function of  $\epsilon$  only. In these calculations we have omitted the sixth-order term, which usually has a small contribution near the transition point. The elastic constant  $C_{44}$  is obtained using the standard definition

$$C_{44}(T) = \frac{\partial^2 \mathcal{F}}{\partial \epsilon^2} = C_{44}^0 - \frac{\delta^2}{\alpha'_3} - \frac{\delta_3^2}{\beta'_1}, \quad (13)$$

where

$$\delta = \delta_4 - \frac{\delta_2 \delta_3}{2\beta'_1}, \quad \alpha'_3 = \alpha_3 - \frac{\delta_2^2}{2\beta'_1} = a_3(T - T'_{c3}), \quad \beta'_1 = \beta_1 - \frac{\delta_1^2}{\beta_2}, \quad (14)$$

with  $T'_{c3} = T_{c3} + \delta_2^2/2\beta'_1$ . The second and third term in Eq. (13) are negative at high temperatures, so both contribute to the softening of  $C_{44}$ . It means that all couplings included in Eq. (1) are involved in this behavior. The main temperature dependence is caused by the second term, but also the last term in Eq. (13) may depend on temperature. In Ref. [10], the softening of  $C_{44}$  was explained taking into account only the bilinear coupling ( $\delta_4$ ). Indeed, if we assume that  $\delta_2 = \delta_3 = 0$ , Eq. (13) reduces to that found in Ref. [10]:  $C_{44} = C_{44}^0 - \delta_4^2/\alpha_3$ . Omitting the last term, Eq. (13) can be written in the form

$$C_{44} = C_{44}^0 \frac{T - T_0}{T - T'_{c3}}, \quad (15)$$

where  $T_0 = T'_{c3} + \delta^2/C_{44}^0 a_3$ . Since, Eq. (15) has the same form as that one discussed in Ref. [10], the fitting procedure will give the following values of parameters:  $T_0 = 66$  K and  $T'_{c3} = 56$  K. Note that the meaning of both temperatures  $T_0$  and  $T'_{c3}$  is here different than in Ref. [10] as they include all interactions. The softening is not complete (only about 10 %) since the first-order phase transition and the change of structure occurs at much higher temperature than  $T_0$ .

### III. DISCUSSION

The present work shows that the VT can be analyzed using the Landau theory of phase transitions. It provides a basis to study the interplay between the OPs and the mechanism of phase transition with two or more OPs. Moreover, majority of experimental facts can be understood in one coherent picture. We emphasize that the coupling between the modes with the  $X_3$  and  $\Delta_5$  symmetry plays the crucial role in the VT in magnetite and explains both the occurrence of the LT monoclinic phase and the metal-insulator transition. This results in rather complex structure of the charge and orbital ordering, with two different charge modulations characterized by  $\mathbf{k}_X$  and  $\mathbf{k}_\Delta$  wave vectors found in diffraction studies [2]. In this work, we have discussed the conditions, which have to be fulfilled for both OPs to develop simultaneously. It depends primarily on the coupling coefficient  $\delta_1$ , which should be negative below  $T_V$  and large enough to stabilize both OPs.

Our present analysis extends also the previous studies of the temperature dependence of  $C_{44}$ . So far, the softening of  $C_{44}$  was studied in the models restricted to the  $\Gamma$  point [10, 11]. Since the phase transition is driven mainly by the OPs at  $\mathbf{k} \neq 0$ , the OPs at the zone center develop solely due to their coupling to other modes. Therefore, the bilinear coupling at the  $\Gamma$  point is rather a side effect of the phase transition, not the main origin of it. The present study shows that also a direct coupling between the  $X_3$  primary OP and the shear strain ( $\delta_3$ ) influences the  $C_{44}$  elastic constant, providing an alternative mechanism of its softening.

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